

CASTABLE POLYURETHANE ELASTOMERS

I.R. CLEMITSON



CRC Press
Taylor & Francis Group

Contents

1	Introduction	1
1.1	What Are Polyurethanes?.....	1
1.1.1	Discovery of Polyurethanes	2
1.2	Polyurethane Family	3
1.2.1	Fibers.....	3
1.2.2	Films	3
1.2.3	Castables Background.....	3
1.2.4	Thermoplastics.....	4
1.2.5	Foams.....	4
1.2.6	Millable.....	4
1.3	Castable Polyurethanes.....	5
1.3.1	Advantages of Polyurethanes	5
1.3.2	Applications.....	5
2	Chemistry	7
2.1	Introduction.....	7
2.1.1	Background.....	7
2.1.2	Basic Reactions of Urethanes	9
2.2	Raw Materials.....	13
2.2.1	Polyols.....	13
2.2.2	Diisocyanates	16
2.2.3	Chain Extenders.....	19
2.2.4	Other Chemicals	23
2.3	Prepolymers.....	24
2.3.1	Commercial Preparation of Prepolymers.....	24
2.3.2	One-Shot System	27
2.4	Urea and Urethane Reactions	28
2.4.1	Introduction.....	28
2.4.2	Speed.....	28
2.5	Chain Extension	29
2.5.1	Urea.....	29
2.5.2	Urethane.....	31
2.5.3	Hydrogen Bonding.....	31
2.5.4	Three-Dimensional Cross-Linking	34
2.5.5	Catalysts	35
2.6	Degradation	37
2.6.1	Prepolymers.....	37
2.6.2	Polyesters.....	39
	References	39

3	Prepolymer Production	41
3.1	Prepolymers	41
	3.1.1 Ease in Production	42
	3.1.2 Isocyanate Levels	42
	3.1.3 Structure of Polyurethane	43
	3.1.4 Reduction in Final Exotherm	43
	3.1.5 Easier Handling of Components.....	43
	3.1.6 Final Properties	43
3.2	Laboratory Preparation	44
	3.2.1 Equipment.....	44
	3.2.2 Reactions	46
	3.2.3 Monitoring Reaction.....	47
	3.2.4 Prepolymer Storage.....	48
3.3	Factory Preparation: Plant Production.....	48
	3.3.1 Safety	48
	3.3.2 Raw Material Storage.....	50
	3.3.3 Raw Material Preparation.....	51
	3.3.4 Reactor	54
	3.3.5 Nitrogen.....	57
	3.3.6 Heating/Cooling	58
	3.3.7 Process Control.....	58
	3.3.8 Vacuum.....	60
	3.3.9 Discharging Batch.....	60
	3.3.10 Quality Control and Assurance.....	61
	3.3.11 Typical Process	63
3.4	Quasiprepolymers.....	64
3.5	One Shot	65
	References	65
4	Hand Processing	67
4.1	Introduction	67
	4.1.1 Process Definition	67
	4.1.2 Importance of the Process.....	67
	4.1.3 Changes in Material Properties Before, During, and After Curing.....	68
	4.1.4 Stages of Curing and Factors Affecting Cure	69
4.2	Introduction to Molding Process	70
	4.2.1 Prepare Mold	72
	4.2.2 Preheat Prepolymer	72
	4.2.3 Add Pigment or Other Additive	72
	4.2.4 Prepare Curative	72
	4.2.5 Mix Prepolymer and Curative	73
	4.2.6 Cast into Mold	73
	4.2.7 Trim Article and Fully Cure Molding in Oven	74
4.3	Casting Health and Safety	74

4.4	Mold Preparation.....	75
4.4.1	Molds	75
4.4.2	Cleaning and Repair.....	76
4.4.3	Mold Release.....	76
4.4.4	Assembly.....	77
4.5	Batch Size Adjustment.....	77
4.5.1	Quantity of Polyurethane.....	77
4.5.2	Weight Calculations.....	77
4.6	Prepolymers.....	78
4.6.1	Calculations	81
4.7	Pigments and Additives	82
4.8	Curatives.....	83
4.9	Degassing	85
4.10	Mixing and Casting	86
4.10.1	Premixing.....	86
4.10.2	Curatives.....	87
4.10.3	Mixing.....	87
4.10.4	Casting.....	88
4.11	Curing and Post Curing	89
5	Processing.....	91
5.1	Molding Methods	91
5.1.1	Rotational Casting	91
5.1.2	Centrifugal Casting.....	92
5.1.3	Vacuum Casting.....	92
5.1.4	Compression Molding.....	93
5.1.5	Liquid Injection.....	94
5.1.6	Complex Shapes.....	94
5.2	Bonding	94
5.2.1	Precasting.....	94
5.2.2	Chemical Treatment	95
5.2.3	Bonding Primer.....	96
5.2.4	Casting and Curing of Bonded Prepolymer	97
5.2.5	Postcasting.....	97
5.3	Finishing	98
5.3.1	Differences from Metals	98
5.3.2	Machining Conditions	99
5.3.3	Painting	101
5.4	Plasticized Polyurethanes	102
5.5	Epoxy-Polyurethane Blends	103
6	Polyurethane Processing Problems.....	105
6.1	Introduction.....	105
6.2	General Problem Solving.....	105
6.2.1	Low NCO Level.....	105
6.2.2	Off Ratio	105

6.2.3	High Exotherm.....	107
6.2.4	Incorrect Temperature.....	107
6.2.5	Curative Contamination.....	108
6.2.6	Poor Mixing.....	108
6.2.7	Casting Technique.....	109
6.2.8	Dirty Molds.....	110
6.2.9	Insufficient Cure.....	110
6.2.10	Low Green Strength.....	110
6.3	Ratios.....	111
6.4	Bond Failure.....	111
6.4.1	Bond Failures at the Metal-to-Primer Interface.....	112
6.4.2	Bond Failures in the Polyurethane-Cement Interface.....	112
7	Properties.....	115
7.1	Introduction.....	115
7.1.1	Type of Backbone.....	115
7.1.2	Backbone Length.....	115
7.1.3	Type of Isocyanate.....	116
7.1.4	Ratio of Reactants.....	116
7.1.5	Type and Concentration of Curative.....	116
7.1.6	Final Processing Conditions.....	117
7.2	Physical Properties.....	117
7.2.1	Temperature.....	117
7.2.2	Resilience.....	118
7.2.3	Thermal Conductivity.....	120
7.2.4	Stress-Strain Properties.....	121
7.2.5	Hardness.....	122
7.2.6	Tensile.....	125
7.2.7	Tear.....	125
7.2.8	Coefficient of Friction.....	126
7.2.9	Compression Set.....	126
7.2.10	Permeability to Water.....	127
7.3	Environmental.....	128
7.3.1	Thermal.....	128
7.3.2	Ozone Resistance.....	130
7.3.3	Hydrolysis.....	130
7.4	Electrical.....	131
7.5	Radiation.....	134
7.6	Chemical.....	134
7.6.1	Inorganic Chemicals.....	134
7.6.2	Organic Chemicals.....	136
7.7	Wear.....	138
7.7.1	Abrasive Wear.....	139
7.7.2	Erosive Wear.....	140
	References.....	144

8	Applications	145
8.1	Introduction	145
8.2	Major Type and Grade Selection	146
8.2.1	Hardness	146
8.2.2	Tear Strength.....	146
8.2.3	Temperature.....	146
8.2.4	Heat Buildup.....	146
8.2.5	Hydrolysis Resistance.....	147
8.2.6	Compression Set.....	147
8.2.7	Tensile Strength.....	147
8.2.8	Oil Resistance	147
8.2.9	Wear Resistance.....	147
8.2.10	FDA Approval.....	147
8.2.11	Flexibility in Adjustments to Formula.....	148
8.2.12	Cost.....	148
8.3	Polyurethane's Role in the Materials Field.....	148
8.3.1	Comparison to Metals	148
8.3.2	Advantages over Plastics	149
8.3.3	Advantages over Rubber.....	150
8.3.4	Limitations of Polyurethanes	151
8.4	Polyurethane Selection Criteria	151
8.4.1	Applications in Tension.....	152
8.4.2	Load Bearing.....	153
8.4.3	Applications in Shear	155
8.4.4	Wear Resistance.....	157
8.4.5	Vibration Damping	158
8.4.6	Electrical.....	158
8.5	Design.....	159
8.5.1	Bonding	159
8.5.2	Fillets.....	159
8.5.3	Shape.....	160
8.6	Summary	161
9	Tools for Evaluation	163
9.1	Introduction	163
9.2	Verification of Selected Grade	164
9.3	Quality Control Tests.....	164
9.3.1	Weighing Equipment.....	164
9.3.2	Temperature.....	164
9.3.3	Linear Dimensions.....	165
9.3.4	Density.....	165
9.3.5	Hardness	166
9.3.6	Curative Level.....	167
9.3.7	Surface Porosity.....	168

9.4	Type Tests	169
9.4.1	Tensile Stress-Strain.....	169
9.4.2	Set Tension Compression.....	170
9.4.3	Tear Strength.....	172
9.4.4	Adhesion	173
9.4.5	Peel Tests	174
9.4.6	Shear Tests.....	175
9.4.7	Compression Modulus.....	176
9.4.8	Shear Modulus.....	177
9.4.9	Dynamic Mechanical Testing.....	177
9.4.10	Resilience.....	178
9.4.11	Dynamic Mechanical Analysis (DMA).....	180
9.4.12	Electrical Properties.....	181
9.4.13	Environmental Resistance	182
9.4.14	Chemical.....	182
9.4.15	Heat Aging.....	184
9.4.16	Fungal.....	185
9.4.17	Wear Resistance.....	185
9.4.18	Dynamic Heat Buildup	187
9.5	Prototype and Service Tests.....	187
9.5.1	First Part Evaluation.....	188
9.5.2	Verification of Design.....	188
9.5.3	Simulated Tests.....	188
9.5.4	Field Trials.....	189
9.6	Investigative Research.....	189
9.6.1	Infrared Studies.....	189
9.6.2	Gas Chromatography	192
9.6.3	Nuclear Magnetic Resonance (NMR).....	192
9.6.4	X-Ray Diffraction	192
9.6.5	Differential Scanning Calorimetry (DSC).....	192
9.6.6	Atomic Force Microscopy	193
9.6.7	Scanning Electron Microscopy (SEM)	193
9.6.8	High Performance Liquid Chromatography (HPLC).....	193
9.6.9	Size Exclusion Chromatography.....	193
References	194
10	Health and Safety	195
10.1	Introduction	195
10.1.1	Rationale.....	195
10.1.2	Work Environment	195
10.1.3	Acute Exposure	196
10.1.4	Chronic Exposure	196
10.2	The Workplace	196
10.2.1	Information Sources	196

10.3	Prepolymer Preparation	199
10.3.1	Isocyanates	199
10.3.2	Polyols	199
10.3.3	Prepolymers	200
10.3.4	Curatives	200
10.3.5	Catalysts	201
10.3.6	Other Additives	202
10.3.7	Solvents	203
10.3.8	Heat	203
10.3.9	Products of Combustion	204
10.4	Engineering	204
10.4.1	Gases	204
10.4.2	Machinery	205
10.5	Material Safety Data Sheet Format	207
	References	210
	Appendix 1 Abbreviations and Trade Names	211
	Appendix 2 Polyurethane Curatives	213
	Appendix 3 Mold Release Agents	215
	Appendix 4 Technical Terms	217
	Appendix 5 Calculations	227
	Appendix 6 Isocyanate Calculation	233
	Appendix 7 Chemical Structures	235
	Appendix 8 Applications	241
	Index	243